

Nano/micro-structured materials: Synthesis, Morphology and Applications

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ABSTRACT

Materials with structural elements, clusters and crystallites or molecules with size dimension in the range 1 -100 nm and /or 4 -20 Å have found potential and real applications as antimicrobial agents, catalysts, nano-filters in waste water treatments and scale forming ions removal etc. These nano/micro-structured materials possess large surface area which is one of the most important properties needed in different fields of applications. In this short review, the different protocols available for the synthesis ranging from green chemistry to chemical reduction methods, structural characterization, morphology and applications of nanostructured materials such as layered double hydroxides, silver and molybdenum oxides have been discussed.

INTRODUCTION

The synthesis of inorganic nanostructured materials, their stabilization, morphology and properties are the main issues of interest in different research groups. The interest is not only for their applications in chemical technology, catalysis, magnetic data storage and sensing (Caruso, 2004), but also for their antimicrobial activities and waste-water treatment. More often than not, marine sediments and aquatic environments are contaminated by urban runoffs, industrial and domestic effluents and oil spills (Goldenberg, 2010). The presence of such contaminants as polycyclic aromatic hydrocarbons (PAHs), poly chlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and heavy metals like mercury, lead and manganese poses risk to both human health and the aquatic biota (Zahir, Rizwi, Hag & Khan, 2005). Functionalized magnetic metal oxide nanoparticles (USEP, 2009, Moffat, Williams, Webb & Stirling, 1994), silver nanoparticles as well as nanostructured layered double hydroxides have proven useful in the remediation of toxic waste in the water environment, inhibition of bacterial and fungi activities (Ashishie, Inah & Ayi, 2018) and removal of scale forming ions from oil wells (Khansi, Anyama, Ayi & Onwuka, 2018).

Different protocols have been employed in the synthesis of nanostructured materials by different research groups.

These synthetic protocols are generally grouped into two categories: “top-down” and “bottom-up” approach. In the top-down approach (milling or attrition), bulk solid is broken into smaller and smaller portions, until nanometer size is reached. The bottom-up method of nanoparticle synthesis involves nucleation of atoms followed by their growth in a self-assembly fashion to form the nanomaterial. Here we will look at the different nanostructured materials prepared by bottom-up methods such as hydrothermal (Chen, Ma, Zhao & Qi, 1995; Ge *et al.*, 2009), combustion synthesis (Kitamura, *et al.*, 2007), gas-phase methods (Jones & Chalker, 2003; Wang *et al.*, 2005), microwave synthesis and sol-gel processing (Watson *et al.*, 2004).

MATERIALS AND METHODS

Nano/micro-structured materials

Nanostructured layered double hydroxides

Layered double hydroxides (LDHs) with the hydrotalcite-like structure are materials attracting interest to many research groups due to their use in many different fields, such as anion scavengers, catalysts, catalyst precursors, hosts for drugs controlled delivery, contaminant and radionuclide removal from acidic mine pit water etc. (Douglas, Shackleton & Woods, 2014; Douglas, 2014; Balsamo *et al.*, 2012). Layered double hydroxides (LDHs) are a class of anionic clays with the structure based on brucite ($\text{Mg}(\text{OH})_2$)-like layers (Cavini, Trifiroa & Vaccaria, 1991; Rives, 2001; Khan & O'Hare, 2012; Sideris *et al.*, 2008; Scarpellini *et al.*, 2015).

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The lattice structure of LDHs with the general formula $[M_{2+1-x}M_{3+x}(OH)_2]^{x+}(A_n^-)_{x/n} \cdot yH_2O$, have a positively charged brucite-shaped layers, consisting of a divalent metal ion M^{2+} (e.g., Ca^{2+} , Zn^{2+} , Mg^{2+} or Ni^{2+}) octahedrally surrounded by six hydroxyl groups (Yang et al., 2016; Everaert et al., 2016; Bao et al., 2016). The substitution of the M^{2+} metal with a trivalent M^{3+} cation gives rise to the periodic repetition of positively charged sheets (lamellas) alternating with charge-counter balancing A_n^- ions. According to Kovačević et al. 2013, synthetic layered double hydroxides (LDHs) have been used as adsorbents and catalyst supports. The surface area and pore volume of LDHs can be increased by pillaring the interlayer with large organic and inorganic anions (Rives and Ulbarri, 1999; Khan and O'Hare, 2002; Kopka et al., 1988).

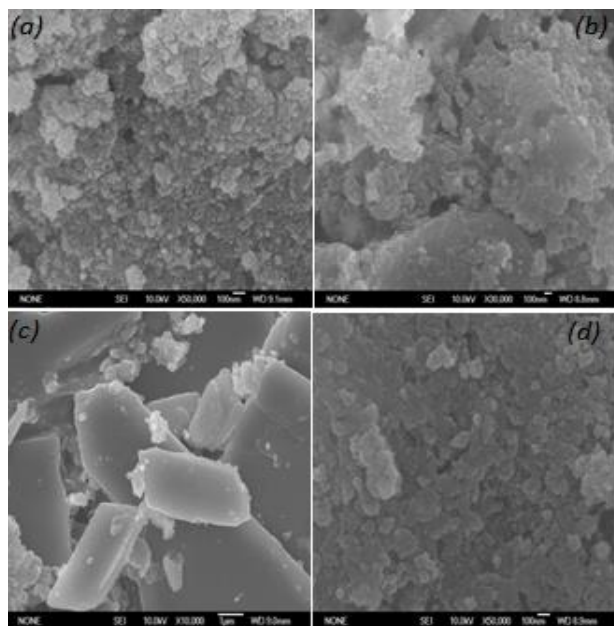


Fig. 1. SEM images of LDHs (a) $Mg-Al(OH)_2PO_4$, 1 (b) $Mg-Al(OH)_2PO_4PF_6$, 2 (c) $Ca-Al(OH)_2SO_4$, 3 and (d) $Ca-Al(OH)_2PO_4PF_6$, 4. (Khansi et al., 2018)

The combination of LDHs with negatively charged polymers such as polystyrene sulfonate can result in the formation of a hybrid layer component for the preparation of nano-hybrid thin films (Hornok et al., 2005; Aradi et al., 2007; Tsyganok et al., 2003). When LDHs which are formed by incorporating both divalent and trivalent metal ions into the octahedral lattice, are calcined at higher temperature, mixed metal oxide nanomaterials are formed with

improved catalytic activity (Choy et al., 2007; Bhattacharjee et al., 2004; Aisawa et al., 2005). LDHs are also used as supports in bio-nanocomposites for medical applications (Yang, Yang & Zhang, 2006).

Khansi et al. 2018, synthesized four metal-aluminum layered double hydroxides (LDHs): $Mg-Al(OH)_2PO_4$, 1, $Mg-Al(OH)_2PO_4PF_6$, 2, $Ca-Al(OH)_2SO_4$, 3 and $Ca-Al(OH)_2PO_4PF_6$, 4, by co-precipitation method followed by mild hydrothermal processing at $60^\circ C$. In Figure 1, we present the SEM micrographs of the as-synthesized LDHs. The synthesized nano-/microstructured LDHs of $Mg-Al(OH)_2PO_4$, 1 (Fig1a), $[Mg-Al(OH)_2PO_4PF_6]$, 2 (Fig.1b) and $[Ca-Al(OH)_2PO_4PF_6]$ 4 (Fig. 1d) have their $Mg-O-Al-OH$ and $Ca-O-Al-OH$ layers intercalated with PO_4^{3-} and / or $[PO_4PF_6]^{4-}$ anions.

RESULTS

Their micrographs consists of uniformed nano/microspheres of $M-Al$ layered double hydroxides, while the $Ca-O-Al-OH$ layer intercalated with SO_4^{2-} anions (Fig.1c) consisted of hexagonal nano-/microplates. The results of the column adsorption studies showed that there is significant potential for using the synthesized nanostructured LDHs as nano filters in removing ions responsible for scale formation in oil wells. According to their report, compounds 1 and 2 removed Fe^{2+} with greater efficiency, while all the synthesized LDHs nanostructures effectively removed Ca^{2+} from the oil wells as shown in Figure 2.

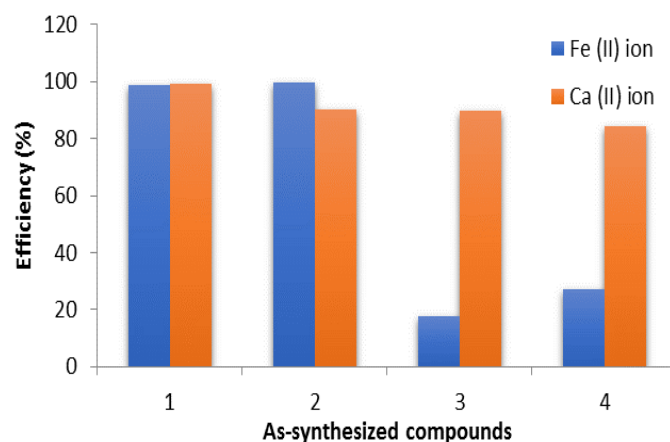


Fig. 2. Results for the removal of Fe^{2+} and Ca^{2+} ions from aqueous solutions by compounds 1-4 Source : Khansi et al. [7]

Nanostructured metal phosphonates

A surfactant-assisted synthesis route to prepare nanometer-sized metal phosphonate particles for use as an inhibitor in porous media for scale control have been reported (Zhang *et al.*, 2009; Shen *et al.*, 2008). In their method, aqueous solution of calcium chloride and zinc chloride were mixed with basic solution containing phosphonate scale inhibitors such as diethylenediamine penta-(methylene phosphonic acid) (DTMP) in the presence of sodium dodecyl sulfate as surfactant. Following similar procedure, Ogar 2015, used hydrothermal technique in the preparation of five nanostructured metal phosphonates. In a typical synthesis, 1.5 g of sodium dodecyl sulphate (SDS) was added to 40 cm³ of 0.25 M solution of the CaCl₂. This was accompanied by constant stirring for 20 minutes (pH = 6). Then 25 cm³ of 1.0 M solution of phenylphosphonic acid (pH = 2) was added dropwise to the above solution with constant stirring. The mixture (pH = 3) was allowed to stir for one hour after which it was transferred into ACE glass tubes and heated for eight hours at a temperature of 120°C. This was followed by centrifugation at 2000 RPM for 20 minutes, filtration and drying of the nanomaterials in an electric incubator at 80°C.

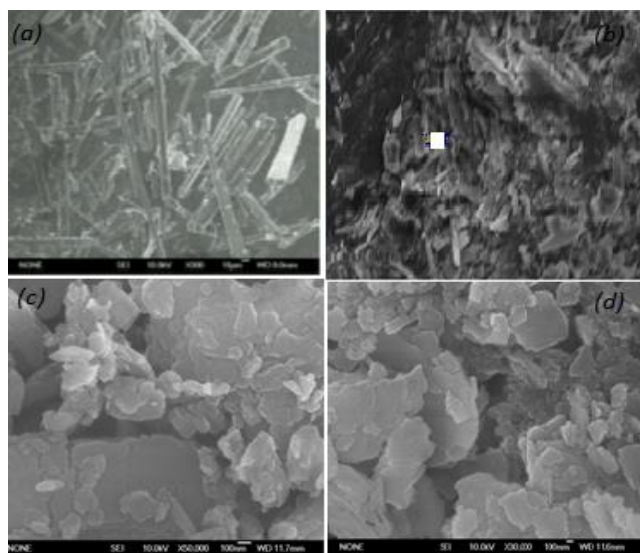


Fig. 3. Representative SEM micrographs (a) UCIM-1 (b) UCIM-2 (c) UCIM-3 (d) UCIM-4

The product obtained was designated UCIM-1, (University of Calabar Inorganic Material). Similar procedure was employed in the synthesis of UCIM-2, UCIM-3, UCIM-4 and UCIM-5 with different complexing agent as aminomethylphosphonic acid

(AmMePhA), 4,4'-biphenyl-bis-phosphonic acid (BBPhA) and different metal salt such as zinc acetate, zinc nitrate or zinc chloride. The SEM micrographs of UCIM-1 and UCIM-2 showed clusters of micro-rods (Figure 3a & b). The zinc phosphonates prepared in the presence of surfactant, UCIM-3 consisted of particles in the size range of 30 – 100 nm (Figure 3c), whereas UCIM-4 and UCIM-5 prepared without the surfactant consists of monodispersed nanoballs (Figure 3d and 3e). The synthesized nanostructured zinc and calcium phosphonates were applied in the removal of scale-forming ions from aqueous solution. A similar procedure reported for LDHs (Khansi *et al.*, 2018) was used. Small amount of glass wool was first introduced into the syringe followed by 0.2 g of the nanoparticles. Two molar solution of CaCl₂ was then introduced. The set-up was left for 12 h during which the solution eluted was collected in sample bottles and analysed using AAS. This was repeated for FeSO₄·7H₂O. The removal efficiency of Fe²⁺ and Ca²⁺ by metal phosphonate nanoparticles (UCIM-n) in percentage was calculated using the formula: Efficiency (%) = $\frac{C_0 - C_e}{C_0} \times 100$ (C₀ = initial concentration of the ions, C_e = eluted concentration of the ions after passing through the packed column).

TABLE 1. Removal efficiency of Ca²⁺ by the synthesized metal phosphonate nanoparticles (Source: Ogar, 2015)

Nanoparticles	Initial amount(ppm)	Amount eluted(ppm)	Amount adsorbed(ppm)	Percentage adsorption
UCIM-1	7.7780	0.4438	7.3342	94.29
UCIM-2	7.7780	1.1512	6.6268	85.20
UCIM-3	7.7780	1.0251	6.7529	86.82
UCIM-4	7.7780	0.5729	7.2051	92.63
UCIM-5	7.7780	0.2399	7.5381	96.92

TABLE 2. Removal efficiency of Fe²⁺ by the synthesized metal phosphonate nanoparticles (Source: Ogar, 2015)

Nanoparticles	Initial amount(ppm)	Amount eluted(ppm)	Amount adsorbed(ppm)	Percentage adsorption
UCIM-1	9.8526	4.1779	5.6747	57.60
UCIM-2	9.8526	5.1040	4.7486	45.46
UCIM-3	9.8526	5.3979	4.4547	45.21
UCIM-4	9.8526	0.7843	9.0683	92.04
UCIM-5	9.8526	0.2399	7.5381	96.92

The removal efficiency of scale forming ions in oil wells by the synthesized metal phosphonate nanoparticles was studied with the help of Atomic Absorption Spectroscopic technique. The removal efficiency of Ca^{2+} and Fe^{2+} ions are presented in Tables 1 and 2 respectively. The results showed that the surfactant-assisted zinc nanostructured material (UCIM-4) removed up to 92.04 % of Fe^{2+} compared to UCIM-5 prepared without surfactant, which showed only 75.88 % removal. The compound UCIM-4 adsorbed Ca^{2+} the most, followed by surfactant-assisted UCIM-1. Ca -nanoparticles with a very high percentage adsorption of 94.29 as presented in Figure 4.

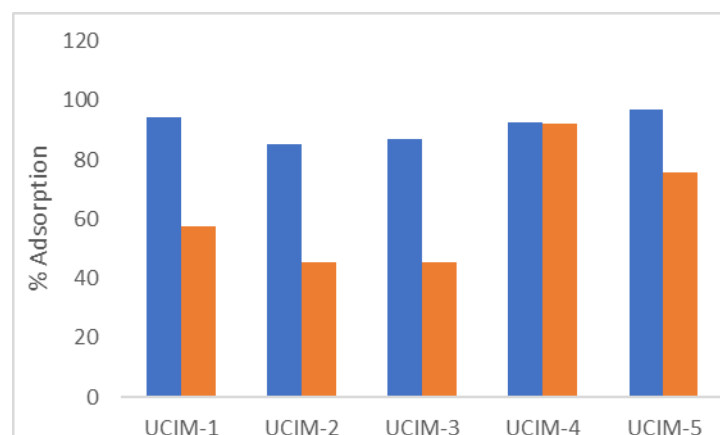


Fig. 4. Bar chart showing percentage adsorption of Ca^{2+} and Fe^{2+} by the different metal phosphonate nanoparticles (Source: Ogar, 2015)

Metal / bimetallic/ metal-oxide nanoparticles

There are a number of interesting reports on the use of ionic liquids as a solvent and/or stabilizing agent in the synthesis of metal/metal-oxide nanoparticles. The interest is not only due to the fact that ILs can form extended hydrogen-bond networks at the liquid state, but also for their nanostructural organization which is being used as a driver for spontaneous formation of nanostructured materials (Bansal & Bhargava, 2011). Khare *et al.*, 2010 reported on the effects of a set of ILs based on the 1-ethyl-3-methylimidazolium cation and different anions on the formation of gold nanoparticles. They demonstrated that the nature of the ionic liquid anion was crucial in the synthesis of the gold nanoparticles. For instance, anions such as methanesulfonate (MS) and

trifluoromethanesulfonate (TfO) stabilized the formation of particles in the size range of 5-7 nm at low temperature, whereas with ethylsulfate (ES), polydispersed particles in the size range 15 - 20 nm were formed at all reaction temperature. In their report, they concluded that specific IL-gold interactions were responsible for the formation of gold particles with an IL-specific shape, size, and aggregation behaviour.

Ayi *et al.* 2010 reported on a wet chemical approach in synthesizing titanium nanoparticles in imidazolium-based ionic liquids (ILs) under reducing conditions. It was established that nanosize particles were formed with some ILs being adsorbed on the nanoparticles, thus providing the needed stabilization.

In continuation of the work on anion effects on nanoparticles formation, stable Mo and molybdenum oxide nano- and microparticles were synthesized in ILs with a variety of anions under reducing conditions by Ayi *et al.*, 2015. XRD and TEM revealed a strong influence of the IL anion on the particle sizes, shapes, and crystal structures. The influence of the IL cation and the reaction temperature was found to be much less pronounced.

Very recently, Ayi's research group have used plant extracts (*K. africana* fruits) to prepare silver nanoparticles and copper-silver bimetallic nanostructures and their antimicrobial potentials evaluated (Ashishie *et al.*, 2018). The aqueous extract of *Kigelia Africana* was utilized in the synthesis of both metallic and bimetallic nanoparticles without additional stabilizing agent. The investigation revealed that average particle size of 10 nm were formed and stabilized by the active components of the plant extract, which were adsorbed on the surface of the particles. The synthesized particles were found to inhibit the growth of both Gram-negative and Gram-positive bacteria more than any of antibiotics tested in the study. The bimetallic nanoparticles demonstrated effectiveness against *S. aureus* with maximum ZOI of 27 mm. John *et al.* 2019 made use of 1-ethyl-3-methylimidazolium acetate (EMIMOAC) and 1-butyl-3-methylimidazolium acetate (BMIMOAC) ionic liquids to prepare cobalt nanoparticles (CoEMIMOAC or CoBMIMOAC) via chemical reduction method.

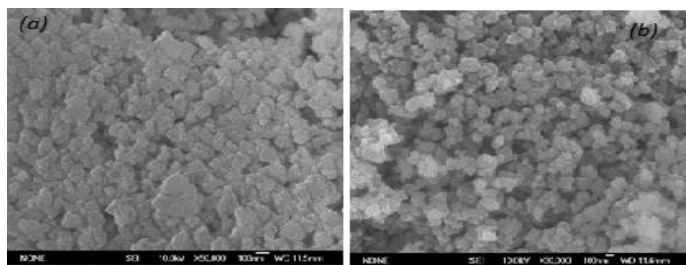


Fig. 5. SEM images of particles grown in (a) EMIMOAC (b) BMIMOAC

The SEM and UV-Vis techniques confirmed the formation of nanoparticles (Figure 5). There was no difference between the nanocrystals formed in EMIMOAC or BMIMOAC indicating that the cationic part of the ionic liquid did not play significant role during nucleation and growth of the particles. The inhibition zone diameter (IZD) showed moderate susceptibility of the *Staphylococcus aureus* to CoBMIMOAC (15 mm) but high susceptibility to CoEMIMOAC with a larger inhibition zone diameter of 23 mm. Gram-negative microorganism *E. coli* is moderately susceptible to both CoEMIMOAC (14 mm), and CoBMIMOAC (15 mm) (Figure 6).

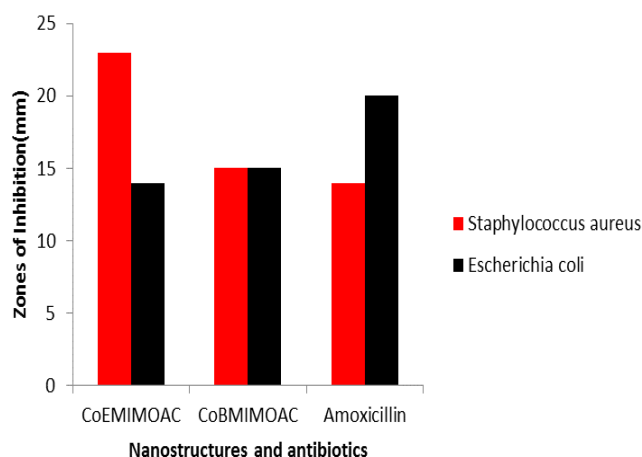


Fig. 6. Bar chart showing nanocrystals inhibition zone diameter for *Staphylococcus aureus* and *Escherichia coli* (Source: John et al., 2019)

CONCLUSION

In this short review, the different protocols available for the synthesis of nanostructured layered double hydroxides and metal phosphonates formulated as UCIM-n have been discussed with

their applications in the removal of scale forming ions from aqueous solutions. Reports of the work done in our research laboratory on green chemistry involving the use of plant extracts and ionic liquids as solvent and stabilizing agents in the syntheses of metal nanoparticles along with their antimicrobial activities have been presented.

ACKNOWLEDGEMENT

This work was supported by The World Academy of Sciences for the Advancement of Science in developing countries (TWAS) under Research Grant No 12-169 RG/CHE/AF/AC-G UNESCO FR: 3240271320 for which grateful acknowledgment is made. A.A.A is also grateful to the Royal Society of Chemistry for personal Research grant. The assistance of Professor J -G. Mao of Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, in the XRD and SEM analyses is gratefully acknowledged.

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